Reaction of Tetraacetatochlorodiruthenium(II,III) with Pyridine-2-carboxylic Acid. X-Ray Crystal Structures of Tris(pyridine-2-carboxylato-κ*N*,*O*)ruthenium(III) Monohydrate and *trans*-Bis(pyridine-2-carboxylato-κ*N*,*O*)bis(triphenylphosphine)ruthenium(II)–Methanol(1/2)†

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The reaction of $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ with pyridine-2-carboxylic acid (Hpyca) in methanol–water (1:1) affords a ruthenium(III) complex, $[Ru(pyca)_3]\cdot H_2O$ **1**, and a diruthenium(II) compound, $[Ru_2(pyca)_4]$ **2**. The reaction of both complexes with PPh_3 leads to the new compound $[Ru(pyca)_2(PPh_3)_2]\cdot 2MeOH$ **3**. The crystal structures of **1** and **3** have been determined. Crystals of both are monoclinic: **1**, space group $C2/c$, $a = 30.415(7)$, $b = 8.506(1)$, $c = 13.943(3)$ Å, $\beta = 94.55(2)°$, $Z = 8$; **3**, space group $P2_1/n$, $a = 9.578(1)$, $b = 20.540(3)$, $c = 11.501(2)$ Å, $\beta = 98.57(1)°$, $Z = 2$. Compound **1** consists of $Ru(pyca)_3$ units linked by water molecules; the ruthenium environment is pseudo-octahedral with the ligands giving a *mer* arrangement. Compound **3** shows a *trans* disposition for the phosphine ligands with the pyridine-2-carboxylate ligands in the equatorial plane. In these complexes the pyridine-2-carboxylate ligands are co-ordinated in a bidentate mode through a carboxylate O atom and the pyridine nitrogen.

The interchange reactions of $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ with several ligands have been used in the synthesis of new $[Ru_2ClL_4]$ complexes (L = mononegative bidentate ligand).[1-16] With unsymmetrical ligands such as CF_3CONH_2,[1,2] $4\text{-}ClC_6H_4CONH_2$,[3] 2-hydroxypyridine,[4] aminopyridines,[4,5] 6-chloro-2-hydroxypyridine,[6] *etc.*, the usual method of synthesis is the reaction of $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ with the molten ligand at elevated temperatures. This procedure is useful when the replaceable hydrogen of the entering ligand is acidic enough to interchange with the acetate of $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$, but requires the use of solid ligands.

Other methods used in the synthesis of these compounds are the reactions of $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ with arene- or alkanecarboxylic acids in water,[7,8] alcohol[9-11] or methanol–water,[12,13] but these reactions sometimes lead to unexpected compounds. For example, with L-mandelic acid (phenylglycolic acid), the chlorotetramandelatodiruthenium(II,III) complex formed is unstable, undergoing a disproportionation reaction which leads to a ruthenium(II) dimer and an oxo-centred ruthenium(III) trimer.[14]

Sometimes, the reduction of $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ occurs, giving ruthenium(II) dimers, although the nature of the reducing agent remains unclear. Thus, the reaction of $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ with excess of 1,3-diaryltriazene in the presence of NEt_3 gives $[Ru_2(RN_3R)_4]$ (R = aryl);[15] the reaction with the sodium salt of 6-methyl-2-hydroxypyridine leads to $[Ru_2(MeNC_5H_3O\text{-}2)_4]$ in 8% yield[16] and with 2,7-bis(2-pyridyl)-1,8-naphthyridine (L) gives $[Ru_2(\mu\text{-}O_2CMe)_3L]PF_6$.[17]

In this paper, we describe the reaction of $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ with pyridine-2-carboxylic acid (Hpyca). The reactivity towards triphenylphosphine of the compounds obtained was also studied.

Results and Discussion

When Hpyca was added to a brown solution of $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ in hot methanol–water (1:1), the colour of the solution changed to dark red in 1 h. From this solution a yellow compound of Ru^{III}, $[Ru(pyca)_3]\cdot H_2O$ **1**, and a red compound of Ru^{II}, $[Ru_2(pyca)_4]$ **2**, can be isolated. Thus, this reaction, can be regarded as a disproportionation process of the Ru_2^{5+} unit. To our knowledge, only three types of disproportionation reactions of the $[Ru_2(\mu\text{-}O_2CMe)_4]^+$ unit have been described in the literature.[14,18,19] In these cases, the ruthenium(III) complex formed is always polynuclear. Unlike these results, in the reaction of $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ with pyridine-2-carboxylic acid a mononuclear ruthenium(III) compound **1** is obtained.

The yellow product **1** is stable to air and moisture, insoluble in the usual organic solvents, and partially soluble in polar solvents such as hot methanol, dimethylsulphoxide, *etc.* The synthesis of this compound, from $K_2[RuCl_5(H_2O)]$, pyridine-2-carboxylic acid and K_2CO_3 in water, has recently been described,[20] showing in the IR spectrum a strong band at 3440 cm^{-1}; however, in the IR spectrum of our sample, which is well crystalline, two strong bands at 3540 and 3460 cm^{-1} can be observed (Table 1). These bands are typical of water molecules attached by hydrogen bonds.

The structure of this compound has been determined by X-ray crystallography and an ORTEP view[21] of the molecular structure is shown in Fig. 1. Selected bond distances and angles are given in Table 2. The co-ordination sphere

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Analytical data and physical properties for the ruthenium complexes

	Analysis (%)[a]			IR (cm^{-1})[b]				
Compound	C	H	N	ν_{asym}	ν_{sym}	$\Delta\nu$	$\nu(H_2O)$	μ_{eff}
1	44.5 (44.5)	2.6 (2.9)	8.3 (8.7)	1660s	1310s	340	3540s 3460s	1.72
2	41.5 (41.7)	2.9 (2.3)	7.8 (8.1)	1660s	1315s	345		2.10
3	64.1 (64.3)	4.8 (5.0)	3.1 (3.0)	1635s	1330s	305		Diamagnetic

[a] Required values are given in parentheses. [b] s = Strong.

Table 2 Bond lengths (Å) and angles (°) for $[Ru(pyca)_3]\cdot H_2O$

Ru–N(1)	2.052(3)	N(2)–C(12)	1.322(5)	C(1)–C(2)	1.504(6)	C(11)–C(12)	1.389(6)
Ru–N(2)	2.064(3)	N(3)–C(14)	1.342(5)	C(2)–C(3)	1.371(6)	C(13)–C(14)	1.507(6)
Ru–N(3)	2.052(3)	N(3)–C(18)	1.348(5)	C(3)–C(4)	1.376(7)	C(14)–C(15)	1.371(6)
Ru–O(1)	2.002(3)	O(1)–C(1)	1.294(5)	C(4)–C(5)	1.374(7)	C(15)–C(16)	1.395(7)
Ru–O(3)	2.024(3)	O(2)–C(1)	1.215(5)	C(5)–C(6)	1.382(6)	C(16)–C(17)	1.368(6)
Ru–O(5)	1.996(2)	O(3)–C(7)	1.288(5)	C(7)–C(8)	1.498(5)	C(17)–C(18)	1.383(6)
N(1)–C(2)	1.348(5)	O(4)–C(7)	1.221(5)	C(8)–C(9)	1.383(6)	O(7)–H(71)	1.165(4)
N(1)–C(6)	1.343(5)	O(5)–C(13)	1.313(5)	C(9)–C(10)	1.389(6)	O(7)–H(72)	1.043(3)
N(2)–C(8)	1.357(5)	O(6)–C(13)	1.207(5)	C(10)–C(11)	1.367(7)		
O(3)–Ru–O(5)	175.9(1)	Ru–N(1)–C(6)	129.8(3)	O(1)–C(1)–C(2)	115.9(3)	C(9)–C(10)–C(11)	118.4(4)
O(1)–Ru–O(5)	93.4(1)	Ru–N(1)–C(2)	111.7(2)	N(1)–C(2)–C(1)	115.0(3)	C(10)–C(11)–C(12)	119.8(4)
O(1)–Ru–O(3)	90.7(1)	C(2)–N(1)–C(6)	118.4(3)	C(1)–C(2)–C(3)	122.7(3)	N(2)–C(12)–C(11)	122.1(4)
N(3)–Ru–O(5)	80.4(1)	Ru–N(2)–C(12)	127.7(2)	N(1)–C(2)–C(3)	122.2(4)	O(5)–C(13)–O(6)	123.8(4)
N(3)–Ru–O(3)	99.7(1)	Ru–N(2)–C(8)	113.3(2)	C(2)–C(3)–C(4)	119.1(4)	O(6)–C(13)–C(14)	122.1(4)
N(3)–Ru–O(1)	91.2(1)	C(8)–N(2)–C(12)	119.0(3)	C(3)–C(4)–C(5)	119.4(4)	O(5)–C(13)–C(14)	114.1(3)
N(2)–Ru–O(5)	96.8(1)	Ru–N(3)–C(18)	127.8(3)	C(4)–C(5)–C(6)	118.9(4)	N(3)–C(14)–C(13)	115.1(3)
N(2)–Ru–O(3)	79.1(1)	Ru–N(3)–C(14)	113.2(2)	N(1)–C(6)–C(5)	122.0(4)	C(13)–C(14)–C(15)	122.1(4)
N(2)–Ru–O(1)	169.8(1)	C(14)–N(3)–C(18)	118.8(3)	O(3)–C(7)–O(4)	125.1(4)	N(3)–C(14)–C(15)	122.8(4)
N(2)–Ru–N(3)	90.2(1)	Ru–O(1)–C(1)	114.6(2)	O(4)–C(7)–C(8)	120.8(4)	C(14)–C(15)–C(16)	118.0(4)
N(1)–Ru–O(5)	94.7(1)	Ru–O(3)–C(7)	117.7(2)	O(3)–C(7)–C(8)	114.0(3)	C(15)–C(16)–C(17)	119.7(4)
N(1)–Ru–O(3)	85.7(1)	Ru–O(5)–C(13)	116.8(2)	N(2)–C(8)–C(7)	115.1(3)	C(16)–C(17)–C(18)	119.2(4)
N(1)–Ru–O(1)	81.3(1)	O(1)–C(1)–O(2)	124.2(4)	C(7)–C(8)–C(9)	123.5(4)	N(3)–C(18)–C(17)	121.5(4)
N(1)–Ru–N(3)	170.8(1)	O(2)–C(1)–C(2)	119.8(4)	N(2)–C(8)–C(9)	121.4(4)	H(71)–O(7)–H(72)	109.2(3)
N(1)–Ru–N(2)	98.1(1)			C(8)–C(9)–C(10)	119.3(4)		

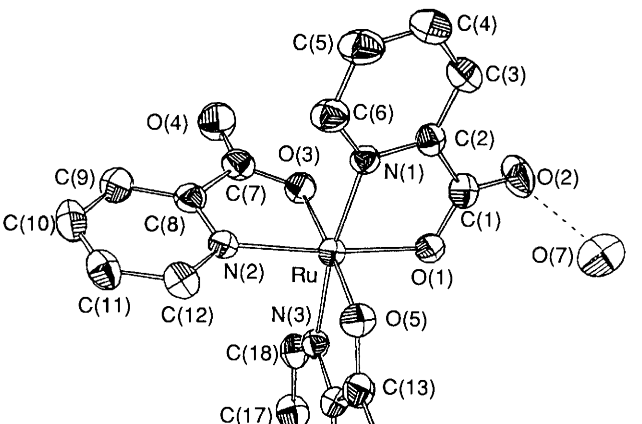

Fig. 1 ORTEP view of $[Ru(pyca)_3]\cdot H_2O$. The hydrogen atoms are omitted for clarity

around the ruthenium atom is approximately octahedral with pyridine-2-carboxylate ligands co-ordinated in a bidentate fashion *via* an oxygen of the carboxylate group and the nitrogen of pyridine, giving a *mer* arrangement. The deviation from 90° of the angle formed by the ruthenium atom with each pyca ligand is caused, primarily, by the formation of the five-membered chelate ring, as in other pyridine-2-carboxylate complexes.[22–24]

The compound crystallizes with one water molecule per $Ru(pyca)_3$ molecule. The oxygen atom of this water molecule is hydrogen bonded to O(2) [2.833(5) Å] of an $Ru(pyca)_3$ molecule and to O(5) [2.878(4) Å] of another $Ru(pyca)_3$ molecule, giving chains in the crystal. Thus, these water molecules act as bridges between different $Ru(pyca)_3$ molecules, making the compound very insoluble.

The red product **2** is stable to air and moisture, insoluble in the usual organic solvents, such as acetone, tetrahydrofuran, toluene, *etc.*, scarcely soluble in methanol and soluble in water. The elemental analysis (C, H and N) is according with the formula $[Ru_2(pyca)_4]$ (Table 1). The IR spectrum shows the absence of bands due to the acetate ligands, indicating that all these groups have been substituted by pyridinecarboxylate ligands. On the other hand, the separation between the symmetric and antisymmetric stretching vibrations of the pyridinecarboxylate ligands in this complex ($\Delta\nu$ = 345 cm^{-1}) clearly indicates that the co-ordination of these ligands to the ruthenium atom occurs *via* an oxygen of the carboxylate group and the nitrogen of pyridine. This separation is analogous to that observed for the compounds $[Ru(pyca)_3]\cdot H_2O$ and $[Ru(pyca)_2(PPh_3)_2]\cdot 2MeOH$ (Table 1) in which the pyca ligand is similarly co-ordinated.

Magnetic measurements at room temperature show an effective magnetic moment of 2.10 corresponding to two unpaired electrons per binuclear unit; this magnetic moment is comparable to those observed for other diruthenium(II) com-

Table 3 Bond lengths (Å) and angles (°) for $[Ru(pyca)_2(PPh_3)_2]\cdot 2MeOH$

Ru–P	2.397(1)	N–C(2)	1.340(8)	C(7)–C(12)	1.366(9)	C(16)–C(17)	1.341(12)
Ru–O(1)	2.102(4)	N–C(6)	1.345(8)	C(8)–C(9)	1.383(10)	C(17)–C(18)	1.398(9)
Ru–N	2.072(5)	C(1)–C(2)	1.508(9)	C(9)–C(10)	1.368(11)	C(19)–C(20)	1.387(9)
P–C(7)	1.840(6)	C(2)–C(3)	1.371(9)	C(10)–C(11)	1.373(11)	C(19)–C(24)	1.380(9)
P–C(13)	1.839(6)	C(3)–C(4)	1.389(11)	C(11)–C(12)	1.404(10)	C(20)–C(21)	1.401(10)
P–C(19)	1.840(6)	C(4)–C(5)	1.373(12)	C(13)–C(14)	1.390(10)	C(21)–C(22)	1.381(12)
O(1)–C(1)	1.283(7)	C(5)–C(6)	1.393(10)	C(13)–C(18)	1.383(9)	C(22)–C(23)	1.355(11)
O(2)–C(1)	1.232(7)	C(7)–C(8)	1.405(9)	C(14)–C(15)	1.396(11)	C(23)–C(24)	1.397(10)
O(3)–C(25)	1.310(10)			C(15)–C(16)	1.390(12)		
O(1)–Ru–N	77.7(2)	C(2)–N–C(6)	118.4(5)	P–C(7)–C(8)	119.9(5)	C(15)–C(16)–C(17)	120.0(7)
P–Ru–N	90.0(1)	O(1)–C(1)–O(2)	124.7(6)	C(8)–C(7)–C(12)	119.8(6)	C(16)–C(17)–C(18)	120.9(7)
P–Ru–O(1)	95.5(1)	O(2)–C(1)–C(2)	120.3(5)	C(7)–C(8)–C(9)	119.4(6)	C(13)–C(18)–C(17)	120.1(6)
Ru–P–C(19)	113.9(2)	O(1)–C(1)–C(2)	115.0(5)	C(8)–C(9)–C(10)	120.5(7)	P–C(19)–C(24)	117.2(4)
Ru–P–C(13)	109.4(2)	N–C(2)–C(1)	115.0(5)	C(9)–C(10)–C(11)	120.6(7)	P–C(19)–C(20)	123.9(5)
Ru–P–C(7)	121.1(2)	C(1)–C(2)–C(3)	122.3(6)	C(10)–C(11)–C(12)	119.5(7)	C(20)–C(19)–C(24)	118.7(6)
C(13)–P–C(19)	105.1(3)	N–C(2)–C(3)	122.5(6)	C(7)–C(12)–C(11)	120.2(6)	C(19)–C(20)–C(21)	119.6(6)
C(7)–P–C(19)	100.2(3)	C(2)–C(3)–C(4)	119.4(6)	P–C(13)–C(18)	117.6(5)	C(20)–C(21)–C(22)	120.8(7)
C(7)–P–C(13)	105.7(3)	C(3)–C(4)–C(5)	118.5(7)	P–C(13)–C(14)	123.1(5)	C(21)–C(22)–C(23)	119.5(7)
Ru–O(1)–C(1)	116.6(4)	C(4)–C(5)–C(6)	119.3(7)	C(14)–C(13)–C(18)	118.9(6)	C(22)–C(23)–C(24)	120.4(7)
Ru–N–C(6)	126.2(4)	N–C(6)–C(5)	121.8(7)	C(13)–C(14)–C(15)	119.9(7)	C(19)–C(24)–C(23)	121.0(6)
Ru–N–C(2)	115.4(4)	P–C(7)–C(12)	120.3(5)	C(14)–C(15)–C(16)	120.0(8)		

Table 4 Summary of crystal data *

	1	3
Formula	$C_{18}H_{14}N_3O_7Ru$	$C_{50}H_{46}N_2O_6P_2Ru$
M	485.4	933.9
Space group	$C2/c$	$P2_1/n$
a/Å	30.415(7)	9.578(1)
b/Å	8.506(1)	20.540(3)
c/Å	13.943(3)	11.501(2)
β/°	94.55(2)	98.57(1)
U/Å^3	3596(1)	2237.3(5)
Z	8	2
F(000)	1944	964
D_c/g cm^{-3}	1.79	1.39
μ/cm^{-1}	9.01	
Crystal dimensions/mm	0.2 × 0.2 × 0.3	0.2 × 0.6 × 0.3
Data collected	(−36, 0, 0) to (36, 10, 16)	(−11, 0, 0) to (11, 24, 13)
Reflections collected	3690	4433
Unique data	3164	3857
Observed data [$I \geqslant 2\sigma(I)$]	2514	3368
R(int)	0.0077	0.078
R	0.025	0.062
R'	0.029	0.072
Average shift/error	0.007	0.02

* Details in common: graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å); monoclinic; 22 °C; ω–2θ scans; three standard reflections every 58.

pounds, so the ground-state configuration of the $[Ru_2(pyca)_4]$ compound could be $\sigma^2\pi^4\delta^2\pi^{*3}\delta^{*1}$.[14,17,25,26]

The low solubility of this compound suggests that the keto group of a carboxylate ligand of the dimer unit may occupy the axial positions of another $Ru_2(pyca)_4$ unit, giving a polymer structure. This behaviour has been observed in other pyridine-2-carboxylate complexes.[27] Unfortunately, all our attempts to obtain single crystals suitable for X-ray crystallography have been unsuccessful.

In the hope of breaking the polymer structure, while maintaining the diruthenium(II) unit, we have carried out the reaction of this red compound with PPh_3 in methanol. In a few minutes, the colour changes from dark red to orange; from this solution, orange crystals of $[Ru(pyca)_2(PPh_3)_2]\cdot 2MeOH$ **3** can be obtained by standing at room temperature or concentration under vacuum. This orange product **3** is also obtained by reaction of the yellow complex **1** with PPh_3 in methanol, and in one step by reaction of $RuCl_3\cdot 3H_2O$, pyridine-2-carboxylic acid, KOH and PPh_3 in methanol, in good yield.

Compound **3** is stable to air and moisture, slightly soluble in polar organic solvents, such as methanol, chloroform, acetone, *etc.* The compound is diamagnetic. The IR spectrum shows bands corresponding to triphenylphosphine and pyridine-2-carboxylate ligands. The separation between symmetric and antisymmetric stretching vibrations is similar to that of the red (**2**) and yellow (**1**) compounds, indicating co-ordination *via* nitrogen and oxygen atoms (Table 1). The ^{1}H NMR spectrum shows three multiplets between δ 7 and 7.5 corresponding to the triphenylphosphine and pyridinecarboxylate ligands. The $^{13}C\text{-}\{^1H\}$ NMR spectrum shows two multiplets at δ 126–134 and 113–125 due to the ring carbons of these ligands and one signal at δ 158.5 due to the carboxylic carbon of the pyca ligand. The $^{31}P\text{-}\{^1H\}$ NMR spectrum shows only one signal at δ 31.97, indicating that all phosphines present in the compound are equivalent.

The elemental analysis (C, H and N) is in accord with the formula $[Ru(pyca)_2(PPh_3)_2]\cdot 2MeOH$, and the spectroscopic data are in accord with a monomeric structure with the phosphine ligands in *trans* positions. However, a dimer structure with four bridging pyridine-2-carboxylate ligands and two phosphine ligands in the axial positions cannot be discounted.

We have determined the crystal structure of this compound by X-ray diffraction, and the monomeric nature has been unequivocally established (Fig. 2). Selected bond lengths and angles are given in Table 3. The crystal structure consists of discrete monomeric centrosymmetric units of the ruthenium complex, with two molecules of methanol of solvation. Some positional disorder around these methanol molecules produces a high *R* value for this compound. The ruthenium environment is pseudo-octahedral, with two phosphines in *trans* positions and two pyridinecarboxylate ligands co-ordinated *via* nitrogen and oxygen atoms. The Ru–P distance is 2.397(1) Å, typical of those found in other triphenylphosphineruthenium(II) complexes.[28–31] The pyridinecarboxylate ligands occupy the equatorial plane.

Experimental

All reactions were carried out in an inert atmosphere, using standard Schlenk techniques. The compounds $RuCl_3\cdot 3H_2O$ (Engelhard), pyridine-2-carboxylic acid (Fluka) and PPh_3 (Merck) were purchased from commercial sources; $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ was prepared by the literature procedure.[32]

Table 5 Atomic parameters for $[Ru(pyca)_3]\cdot H_2O$

Atom	*x*	*y*	*z*
Ru	0.112 864(9)	0.290 374(37)	0.131 911(21)
N(1)	0.168 415(95)	0.425 128(366)	0.160 182(212)
N(2)	0.118 011(93)	0.256 871(346)	−0.013 448(209)
N(3)	0.053 824(98)	0.172 898(360)	0.122 538(209)
O(1)	0.115 003(80)	0.289 549(350)	0.275 832(176)
O(2)	0.160 939(108)	0.335 405(415)	0.404 447(199)
O(3)	0.154 670(84)	0.105 126(328)	0.133 993(182)
O(4)	0.199 476(106)	−0.030 032(414)	0.045 657(233)
O(5)	0.071 694(84)	0.473 219(302)	0.119 649(196)
O(6)	0.001 085(100)	0.541 504(367)	0.119 072(267)
O(7)	0.109 480(120)	0.240 495(410)	0.554 356(280)
C(1)	0.151 127(133)	0.344 591(473)	0.318 376(275)
C(2)	0.181 373(120)	0.427 643(439)	0.254 860(267)
C(3)	0.219 344(136)	0.501 737(539)	0.290 334(306)
C(4)	0.244 409(148)	0.579 707(587)	0.227 568(347)
C(5)	0.230 850(146)	0.582 115(598)	0.131 173(357)
C(6)	0.193 022(135)	0.501 828(564)	0.099 374(304)
C(7)	0.169 724(129)	0.063 978(490)	0.053 926(297)
C(8)	0.147 429(121)	0.143 541(474)	−0.032 694(276)
C(9)	0.155 100(142)	0.104 492(546)	−0.126 180(309)
C(10)	0.132 216(158)	0.182 942(570)	−0.201 969(289)
C(11)	0.102 676(143)	0.296 822(562)	−0.181 092(285)
C(12)	0.096 339(135)	0.331 099(452)	−0.085 773(282)
C(13)	0.029 424(134)	0.442 031(478)	0.119 511(288)
C(14)	0.018 799(116)	0.268 980(467)	0.121 927(255)
C(15)	−0.023 562(126)	0.214 890(563)	0.123 344(294)
C(16)	−0.030 211(140)	0.052 721(566)	0.124 825(317)
C(17)	0.005 235(149)	−0.046 450(518)	0.124 630(314)
C(18)	0.047 096(138)	0.016 258(483)	0.123 313(282)

Table 6 Atomic parameters for $[Ru(pyca)_2(PPh_3)_2]\cdot 2MeOH$

Atom	*x*	*y*	*z*
Ru	0.0000(0)	0.0000(0)	0.5000(0)
P	0.0479(1)	0.0060(1)	0.7103(1)
O(1)	0.0927(4)	0.0901(2)	0.4703(3)
O(2)	0.0547(5)	0.1971(2)	0.4620(4)
O(3)	0.3155(6)	0.1977(3)	0.3828(6)
N	−0.1673(5)	0.0640(2)	0.4998(4)
C(1)	0.0146(6)	0.1407(3)	0.4724(5)
C(2)	−0.1357(6)	0.1271(3)	0.4896(5)
C(3)	−0.2340(8)	0.1756(3)	0.4902(7)
C(4)	−0.3727(8)	0.1593(4)	0.4995(8)
C(5)	−0.4065(7)	0.0947(4)	0.5085(7)
C(6)	−0.3015(6)	0.0478(3)	0.5080(6)
C(7)	0.1701(6)	0.0673(3)	0.7845(5)
C(8)	0.1920(8)	0.0714(3)	0.9078(6)
C(9)	0.2885(8)	0.1158(4)	0.9628(6)
C(10)	0.3600(8)	0.1564(3)	0.8980(7)
C(11)	0.3401(8)	0.1526(4)	0.7775(7)
C(12)	0.2442(7)	0.1070(3)	0.7205(6)
C(13)	−0.1187(6)	0.0172(3)	0.7693(5)
C(14)	−0.1489(7)	0.0726(4)	0.8304(6)
C(15)	−0.2822(8)	0.0802(4)	0.8638(7)
C(16)	−0.3835(8)	0.0318(5)	0.8381(7)
C(17)	−0.3552(7)	−0.0209(4)	0.7768(6)
C(18)	−0.2236(6)	−0.0287(3)	0.7398(6)
C(19)	0.1260(6)	−0.0687(3)	0.7806(5)
C(20)	0.0493(7)	−0.1163(3)	0.8287(6)
C(21)	0.1167(9)	−0.1737(4)	0.8725(7)
C(22)	0.2586(8)	−0.1834(3)	0.8684(6)
C(23)	0.3334(7)	−0.1367(4)	0.8218(6)
C(24)	0.2682(7)	−0.0788(3)	0.7793(6)
C(25)	0.3041(9)	0.2324(4)	0.2863(8)

The ^1H, ^{13}C and ^{31}P NMR spectra were recorded with a Varian VXR-300 spectrometer, using $CDCl_3$ as solvent; ^1H and ^{13}C chemical shifts are relative to $SiMe_4$, ^{31}P relative to external 85% H_3PO_4. Infrared spectra were recorded on a Philips PU 9712 spectrophotometer. Elemental analyses of C, H and N were performed with a Perkin-Elmer 240B Microanalyser. The magnetic measurements were made with a DSM 5 magnetometer at room temperature.

Reaction of $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ *with Pyridine-2-carboxylic Acid.*—To a brown solution of $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ (0.3 g, 0.63 mmol) in methanol–water (1:1, 80 cm^3) was added pyridine-2-carboxylic acid (0.5 g, 3.80 mmol). The mixture was stirred at reflux for 4 h, giving a red solution. This solution was allowed to stand at room temperature and whereupon a yellow solid is slowly formed. The yellow precipitate was filtered off and recrystallized from hot methanol, giving yellow crystals characterized as $[Ru(pyca)_3]\cdot H_2O$.

The red solution was pumped to dryness and the residue washed with $CHCl_3$ (5×10 cm^3) to remove the free acid, giving a red solid characterized as $[Ru_2(pyca)_4]$.

Synthesis of $[Ru(pyca)_2(PPh_3)_2]\cdot 2MeOH$.—*Method* (*a*), *from* $[Ru_2(pyca)_4]$. To a suspension of $[Ru_2(pyca)_4]$ (0.15 g, 0.22 mmol) in methanol (60 cm^3) was added PPh_3 (0.23 g, 0.87 mmol). The reaction mixture was heated at reflux for 2 h, then cooled to room temperature to yield orange crystals. The solution was filtered and the crystals washed with diethyl ether. The compound was recrystallized from hot methanol.

Method (*b*), *from* $[Ru(pyca)_3]\cdot H_2O$. To a solution of $[Ru(pyca)_3]\cdot H_2O$ (0.15 g, 0.31 mmol) in methanol (60 cm^3) was added PPh_3 (0.32 g, 1.24 mmol) and the reaction mixture was refluxed for 4 h. During this time orange crystals formed. The solution was filtered and the crystals were purified by the method described above.

Method (*c*), *from* $RuCl_3\cdot 3H_2O$. To a solution of $RuCl_3\cdot 3H_2O$ (0.15 g, 0.57 mmol) in methanol (25 cm^3) was added a solution NaOH (0.09 g, 2.29 mmol) in methanol (10 cm^3), pyridine-2-carboxylic acid (0.28 g, 2.29 mmol) and PPh_3 (0.60 g, 2.29 mmol). The reaction mixture was heated at reflux for 1 h to obtain orange crystals, which were treated by the method described above.

X-Ray Data Collection and Structure Determination.—The crystals of both compounds were mounted in a Nonius CAD-4 diffractometer. The cell dimensions were initially refined by least-squares fitting of the 2θ values of 25 reflections. There was no appreciable change in the periodically monitored standard reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Ru and P were taken from ref. 33. The crystal data are shown in Table 4.

The heavy atoms of both compounds were located from three-dimensional Patterson maps. The positions of the non-hydrogen atoms were obtained from Fourier synthesis. An empirical absorption correction[34] was applied at the end of the isotropic refinement. Some positional disorder in $[Ru(pyca)_2(PPh_3)_2]\cdot 2MeOH$ was found around the MeOH molecule of crystallization; because of this the atoms C(25) and O(3) of these groups have been refined only isotropically and the R value is higher than for compound **1**. No trend in ΔF *vs.* F_o or $(\sin\theta)/\lambda$ was observed.

Hydrogen atoms were fixed at calculated positions, only those of the water molecule in $[Ru(pyca)_3]\cdot H_2O$ and the MeOH

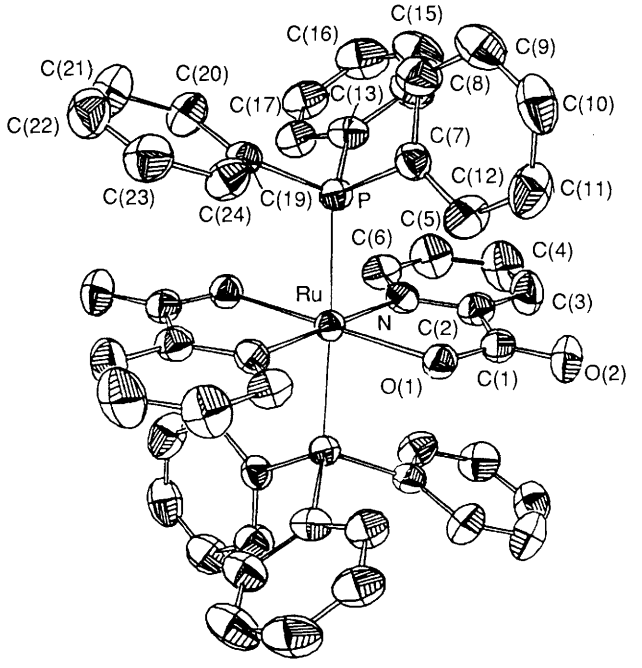

Fig. 2 ORTEP view of [Ru(pyca)$_2$(PPh$_3$)$_2$]·2MeOH. The hydrogen atoms and solvent molecules are omitted for clarity

in [Ru(pyca)$_2$(PPh$_3$)$_2$]·2MeOH were located in a final Fourier difference synthesis as the highest peak and their co-ordinates were subsequently refined. Most of the calculations were carried out with X-RAY 80.[35] The distances and angles are summarized in Tables 2 and 3.[36] Tables 5 and 6 contain the atomic coordinates.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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